to hydrolysis. In oxidation reactions, however, it reacts with vigor. It is oxidized rapidly on exposure to the atmosphere, and although much heat is generated, it does not inflame as has been reported for trifluoromethylphosphonous dichloride.[11]

EXPERIMENTAL

Preparation of tetrachloro(trichloromethyl)phosphorane. A solution of 234 g. (2.0 moles) methylphosphonous dichloride[4] in 600 g. phenylphosphonic dichloride as solvent[12] was stirred at 0° while 149 g. (2.1 moles) chlorine was added. The slurry of tetrachloromethylphosphorane was warmed to 60° and held there by cooling while 490 g. (6.9 moles) chlorine was added over a period of 3 hr. Chlorine consumption was complete until shortly before the stoichiometric amount (6.0 moles) had been added. The slurry was stirred at 55–60° under 100–150 mm. pressure to remove hydrogen chloride and excess chlorine. The product was not isolated but was used directly in the next step.

Preparation of trichloromethylphosphonous dichloride. The above reaction mixture was protected with nitrogen while 266 g. (2.0 moles) methyl phosphorodichloridite was added in 1.5 hr. The use of a small excess of this reagent causes no difficulty, but a large excess appears to reduce the yield. The mild exotherm was controlled to give a reaction temperature of 35°; higher temperatures cause slight yield reduction. Evolution of methyl chloride occurred near the end of the reaction as its solubility in the mixture was exceeded. The resulting clear solution was rectified *in vacuo* with a 0.75 in. by 15 in. column of Hastelloy B Heli-Pak. After a cut of phosphorus oxychloride, a 39-g. fraction, possibly a mixture of the chlorinated methylphosphonous dichlorides,

(11) F. W. Bennett, H. J. Emeléus, and R. N. Haszeldine, *J. Chem. Soc.*, 1565 (1953).

(12) Available from Victor Chemical Works. This compound is inert in the reactions discussed and is used as solvent throughout; its high boiling point (258°) permits its use as a "chaser" in the distillation to isolate trichloromethylphosphonous dichloride. Other inert solvents are also useful.

was obtained over the range 63° at 30 mm. to 70° at 26 mm. Trichloromethylphosphonous dichloride was then collected at 69–70° at 23 mm. There was obtained 375 g. (1.70 moles), a yield of 85% on methylphosphonous dichloride charged. The still bottoms of phenylphosphonic dichloride were recovered for further use by simple distillation.

Trichloromethylphosphonous dichloride freezes at 47°[13] and boils at 171–172°[13] at 750 mm. It must be protected from the atmosphere, as oxidation occurs with great ease. It is insoluble in, and reacts only slowly with, water. It reacts quantitatively with chlorine to form tetrachloro(trichloromethyl)phosphorane.

Anal. Calcd. for CCl_5P: C, 5.45; Cl, 80.48; P, 14.07. Found: C, 5.23; Cl, 80.30; P, 14.33.

Reduction of tetrachloromethylphosphorane with methyl phosphorodichloridite. To a solution of 35.1 g. (0.30 mole) methylphosphonous dichloride in 300 g. chlorobenzene was added 22.0 g. (0.31 mole) chlorine. The temperature was held at 10° during this formation of tetrachloromethylphosphorane. The slurry was then warmed to 50° and treated over a period of 30 min. with 39.5 g. (0.30 mole) methyl phosphorodichloridite. The resulting clear solution was rectified. A 26.9-g. fraction of methylphosphonous dichloride (77% recovery) boiling at 81–82° was collected. In addition, a small forerun (5 g.) boiling from 77–81° was obtained; this probably contained more of the product along with phosphorus trichloride, formed as shown in Equation 3.

Attempted preparation of tetrachloromethoxyphosphorane. A solution of 40 g. (0.30 mole) methyl phosphorodichloridite in 265 ml. chlorobenzene was held below 10° while 22 g. (0.31 mole) chlorine was added. The exothermic reaction was completed in 45 min. Distillation was then conducted at reduced pressure (15–20 mm.) so as to maintain a pot temperature of 30°. Methyl chloride was evolved and collected in a Dry Ice trap. The distillate consisted of phosphorus oxychloride and the solvent. No residue remained after distillation. Tetrachloromethoxyphosphorane was thus shown to be unstable near room temperatures, decomposing cleanly according to Equation 2.

SOUTH CHARLESTON, W. VA.

(13) Uncorrected.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA AND THE RESEARCH DEPARTMENT, STAUFFER CHEMICAL CO.]

Derivatives of Sulfenic Acids. XXXIII. Studies of Thioperoxides. Part 4. Reactions of Trichloromethanesulfenyl Chloride with 1,2-Epoxides and Alcohols

ROBERT B. LANGFORD AND NORMAN KHARASCH

Trichloromethanesulfenyl chloride (I) reacts with 1,2-epoxides and with *meso*-1,2,3,4-diepoxybutane to form *beta*-chloroalkyl trichloromethanesulfenates. The reaction is catalyzed by tertiary amines, and identical products are obtained by substituting appropriate *beta*-chloro alcohols for the epoxides. The results agree with the mechanism which postulates *trans* opening of the epoxide rings, as previously suggested for the similar reactions of 2,4-dinitrobenzenesulfenyl chloride. The new products from reaction of I with epoxides and certain alcohols are reported.

Trichloromethanesulfenyl chloride (I) holds a unique position among aliphatic sulfenyl halides. Historically, it was the first of this group of substances to be reported,[1] its precise structure has
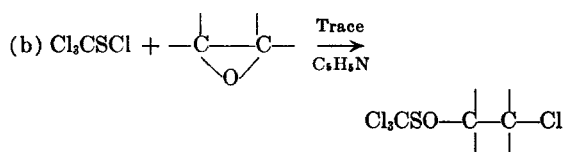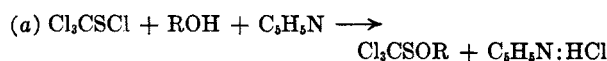
(1) B. Rathke, *Ann.*, 167, 204 (1873); *Cf.* also N. Kharasch, S. J. Potempa, and H. L. Wehrmeister, *Chem. Revs.*, 39, 269 (1946).

been carefully investigated by infrared spectra,[2] and both the sulfenyl chloride and its derivatives have intrigued many industrial investigators.[3]

(2) J. A. A. Ketelaar and W. Vedder, *Rec. trav. chim.*, 74, 1482 (1955).

(3) *Cf. e.g.* (a) A. R. Kittleson and H. L. Yowell, U. S. Patent 2,553,771 (1951); (b) G. H. Birum and R. J. Kern, U. S. Patent 2,769,777 (1956); and (c) E. M. Nygaard and J. H. McCracken, U. S. Patent 2,326,102 (1943).

In the present study, the reactions of I with certain 1,2-epoxides and alcohols were examined, for comparison with the similar reactions of 2,4-dinitrobenzenesulfenyl chloride.[4] The reactions involved were (a) and (b):

(a) $Cl_3CSCl + ROH + C_5H_5N \longrightarrow$
$Cl_3CSOR + C_5H_5N:HCl$

(b) $Cl_3CSCl +$ —C—C— $\xrightarrow[C_5H_5N]{\text{Trace}}$
\O/

Cl_3CSO—C—C—Cl

The products obtained are listed in Table I.

If *trans* opening of the epoxide ring is involved in reaction *b*, the product from 1,2-epoxycyclohexane should be *trans*-2-chlorocyclohexyl trichloromethanesulfenate (II). This was verified by finding that the alcohol obtained by acid hydrolysis of II was *trans*-2-chlorocyclohexanol,[8] and, as expected, the product from reaction of I with 2-chloroethanol was the same as formed with epoxyethane. Since ring opening of the epoxide should follow predictions for acidic openings of such rings (attack by the anion on the protonated epoxide taking place preferentially at a primary carbon rather than at a secondary or tertiary one), the major product from reaction of I and 3-chloro-1,2-epoxypropane should

TABLE I

SYNTHESIS OF TRICHLOROMETHANESULFENATES FROM TRICHLOROMETHANESULFENYL
CHLORIDE AND EPOXIDES OR ALCOHOLS

Epoxide or Alcohol	Yield, %	B.P./Mm.[a]	n_D^{20}	Analyses							
				Calcd.				Found			
				C	H	S	Cl	C	H	S	Cl
Epoxyethane	85	45–46°/0.1	1.5230	15.67	1.75	13.94	61.68	15.72	1.72	13.91	61.59
2-Chloroethanol	59	52–53°/0.2	1.5223	[b]							
1,2-Epoxypropane	83	43–44°/0.1	1.5124	19.69	2.48	13.14	58.13	19.83	1.56	13.10	57.98
1-Chloro-2-propanol	54	53–54°/0.2	1.5106	[b]							
3-Chloro-1,2-epoxypropane	76	75–76°/0.2	1.5321	17.25	1.81	11.51	63.67	17.02	1.50	11.65	63.72
1,3-Dichloro-2-propanol	57	79–80°/0.1	1.5320	[b]							
1,2-Epoxycyclohexane[e]	74	89–90°/0.1	1.5334	29.60	3.55	11.29	49.93	29.53	3.56	11.38	50.09
Phenylepoxyethane[f]	74	119–121°/0.2	1.5270	35.32	2.63	10.48	46.34	35.55	2.57	10.18	46.02
meso-1,2,3,4-Diepoxybutane[g]	24	(m.p. 96–97°)	–	15.74	1.32	·	61.95	15.88	1.33	—	62.10
Methanol[c]	77	53–54°/14	1.5050	13.24	1.66	17.67	58.61	12.93	1.58	18.09	58.45
1-Propanol[c]	52	31–32°/0.3	1.4800	[d]							
2-Propanol[c]	41	32–33°/0.4	1.4820	[d]							
Allyl alcohol[c]	55	52–53°/0.1	1.5413	[d]							
Tetrahydrofurfuryl alcohol[c]	48	74–75°/0.2	1.5180	[d]							

[a] Read from a tilting McLeod gauge. [b] These alcohol derivatives were not analyzed for elementary composition, as they were shown to be identical with the epoxide derivatives by comparison of infrared spectra. [c] Previously reported by Sosnovsky. [d] Not analyzed. Identity verified by infrared spectra. [e] Product is *trans*-2-chlorocyclohexyl trichloromethanesulfenate. [f] Product is 1-phenyl-2-chloroethyl trichloromethanesulfenate. [g] Product is *meso*-1,4-dichloro-2,3-bis(trichloromethanesulfenoxy)butane, III.

Certain of the esters of trichloromethanesulfenic acid are recorded in the literature, having been prepared by the reaction of I with the metallic salt of an alcohol or phenol.[5] The use of pyridine and other tertiary amines as catalytic condensing agents has been reported earlier in this series,[4] and recently, also, for the reaction of I with primary and secondary alcohols.[6] Brintzinger *et al.*,[7] found that the reaction of monochloromethanesulfenyl chloride with two equivalents of epoxyethane took place without the necessity of an added catalyst.

(4) (a) N. Kharasch, D. P. McQuarrie, and C. M. Buess, *J. Am. Chem. Soc.*, **75**, 2658 (1953); (b) L. Goodman and N. Kharasch, *J. Am. Chem. Soc.*, **77**, 6541 (1955); and (c) D. Peters and N. Kharasch, *J. Org. Chem.*, **21**, 590 (1956).

(5) J. M. Connolly and G. M. Dyson, *J. Chem. Soc.*, 822 (1934); *J. Chem. Soc.*, 679 (1935); and *J. Chem. Soc.*, 827 (1937).

(6) G. Sosnovsky, *J. Chem. Soc.*, 3139 (1956).

(7) H. Brintzinger, H. Schmahl, and H. Witte, *Ber.*, **85**, 338 (1952).

be 1,3-dichloro-2-propyl trichloromethanesulfenate, which should also result by reaction of I and 1,3-dichloro-2-propanol. These predictions were verified, since the major product obtained from both routes was identical, as shown by boiling points, refractive indices, and infrared spectra.

The product from *meso*-1,2,3,4-diepoxybutane with I would be expected to be III, *i.e. meso*-1,4-dichloro-2,3-bis(trichloromethanesulfenoxy)-bu-

CH_2Cl
|
HC—$OSCCl_3$
|
HC—$OSCCl_3$
|
CH_2Cl

(III)
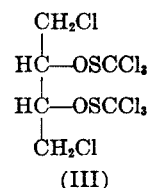
tane. The product isolated from the reaction of the

(8) H. C. Stevens and O. Grummit, *J. Am. Chem. Soc.*, **74**, 4877 (1952).

epoxide[9] and I, mixed in 1:2 molar ratios, gave a glycol, on hydrolysis, which melted at 127°, and was identical with meso-1,4-dichloro-2,3-butanediol, prepared from trans-1,4-dichloro-2-butene by oxidation with peracetic acid[10,11] Permanganate oxidation[12] of the same olefin gave dl-1,4-dichloro-2,3-butanediol, m.p. 62°. Infrared spectra of the glycol obtained from the sulfenyl ester and the meso-1,4-dichloro-2,3-butanediol were identical, but the spectrum of the racemic diol was quite different.

Except for the meso-1,2,3,4-diepoxybutane derivative, which is a white crystalline solid, the esters of Table I, when pure, are water-white liquids which may be distilled at low pressure with very little decomposition. Samples have been kept for over a year in well stoppered containers without noticeable change. Sunlight and heat, however, appear to induce decomposition, although a systematic study of this behavior has not yet been made. Hydrolysis has also been noted on storing poorly stoppered samples, with some of the alcohol being found on redistillation.

It is to be noted that these compounds are related to both disulfides and peroxides, and have been designated also as thioperoxides. The use of some of these substances as agents for inducing the photopolymerization of olefins[3b] undoubtedly shows that they can undergo free-radical decomposition. Certain of these esters also show oxidizing ability toward iodide ion.[13]

Some difficulty was encountered in obtaining good analytical results for the products in Table I, as Barltrop, Hayes, and Calvin have noted.[13] It was found, however, that good analyses were obtained with samples purified by rigorous redistillations through a suitable column.

Triethylamine, and presumably other tertiary amines, may be used in place of pyridine in the reactions of trichloromethanesulfenyl chloride with alcohols and epoxides. The necessity of such a catalyst for the epoxide reaction was demonstrated in the reaction of I with epoxyethane. Although the reaction normally goes to completion within a few hours when a small amount of a tertiary amine is present, no apparent reaction occurred in eight days without a catalyst. On distillation of the reaction mixture, over 95% of the initial amount of I was recovered and no distillate was obtained in the boiling range of the sulfenyl ester.

The infrared spectra of these compounds were obtained in the region from 650 to 10,000 cm.$^{-1}$, and were found to agree with the assigned structure of the products in Table I. The region from 710 to 810 cm.$^{-1}$, in particular, showed the typical curve associated with the trichloromethylthio group in trichloromethanesulfenyl chloride.[2]

In the course of this investigation several of the trichloromethanesulfenates reported by Sosnovsky[6] were prepared. Their identity was confirmed by infrared spectra and by their boiling points which agree quite well with the literature. Although incidental to the primary topic discussed here, they are included in Table I to increase the available information on this series of compounds.

EXPERIMENTAL

Trichloromethanesulfenyl chloride was prepared by redistilling technical grade "perchloromethyl mercaptan," obtained from the Stauffer Chemical Co. Cyclohexene oxide was obtained from Arapahoe Chemicals, Inc., and the other epoxides and alcohols were the product of Distillation Products Industries. With the exception of practical grade 1-chloro-2-propanol, which was carefully fractionated, these were all reagent grade, and were used as supplied. Reagent pyridine, dried over sodium hydroxide, and 1,2-dichloroethane, dried by distillation, were used in these reactions. The infrared spectra were made in carbon disulfide solutions or on the neat liquids, using a Perkin-Elmer double-beam spectrophotometer, Model 21.

General procedure for the reaction of trichloromethanesulfenyl chloride with epoxides. To a solution of 0.10 mole of I in 100 ml. of dry 1,2-dichloroethane was added 0.11 mole of the epoxide. To this mixture 0.5 ml. of dry pyridine was added. Completion of this reaction, which may require several hours, was determined by the disappearance of the odor of I and by a negative starch-iodide test for the presence of I. The mixture was washed with water to remove the amine and amine hydrochloride and dried over anhydrous sodium sulfate. The dried solution was aspirated to remove the solvent and the residue distilled under reduced pressure to obtain the product.

Procedure for the reaction of trichloromethanesulfenyl chloride with 1,2,3,4-diepoxybutane. To a solution of 0.20 mole of I in 100 ml. of dry ethylene chloride was added 0.10 mole of 1,2,3,4-diepoxybutane.[9] To this mixture was added 1.0 ml. of dry pyridine. Although the last trace of I remained after two days, the mixture was water-washed, dried, and aspirated, as in the general procedure above. The residual viscous oil readily dissolved in 200 ml. of methanol, at room temperature. Within a minute, a precipitate of white crystals began to form. After cooling to 0°, the crystals were collected and air-dried (11 g.; 24%); m.p. after recrystallization from methanol, 96–97°.

General procedure for the reaction of trichloromethanesulfenyl chloride with alcohols. To a solution of 0.10 mole of I in 100 ml. of dry 1,2-dichloroethane was added 0.11 mole of the dry alcohol. To this was gradually added, with stirring, 0.11 mole of dry pyridine. Completion of the reaction, which may require several hours, was determined as above, and the product was isolated by fractional distillation.

(9) The 1,2,3,4-diepoxybutane was kindly supplied by Union Carbide Chemicals Co., and was reported to be over 90% meso isomer. This material causes painful blistering on contact with the skin and was also reported possibly carcinogenic.

(10) The identity of the trans-1,4-dichloro-2-butene was verified by comparing its infrared spectrum with that recorded by K. Mislow and H. M. Hellman, J. Am. Chem. Soc., 73, 246 (1951).

(11) D. Swern, G. N. Billen, T. W. Findley, and J. T. Scanlan, J. Am. Chem. Soc., 67, 1787 (1945).

(12) R. M. Evans and L. N. Owen, J. Chem. Soc., 239 (1943).

(13) J. A. Barltrop, P. M. Hayes, and M. Calvin, J. Am. Chem. Soc., 76, 4348 (1954).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE VIRGINIA POLYTECHNIC INSTITUTE]

Unsaturated Cyclic Sulfones. IV. Isomeric 2-Methyldihydrothiophene 1,1-Dioxides

ROBERT C. KRUG AND JAMES A. RIGNEY[1]

2-Methyl-2,5-dihydrothiophene 1,1-dioxide (I) has been carefully characterized, and from this sulfone the remaining two isomeric sulfones have been obtained. Isomerization of I in basic medium gives 2-methyl-4,5-dihydrothiophene 1,1-dioxide and the pyrolysis of the acetate from the alcohol from I gives 2-methyl-2,3-dihydrothiophene 1,1-dioxide.

The characterization of 2-methyl-2,5-dihydrothiophene 1,1-dioxide (I) and the development of reasonably simple methods of preparation of the remaining isomeric sulfones and their subsequent characterization are necessary to the study of the chemistry of the sulfones[2] of the 2-methyl series.

In 1943 Craig[3] reported the preparation of I from the reaction of 1,3-pentadiene and sulfur dioxide, and although he reported that he was able to distill the sulfone no physical constants were given for this product. In 1945 Morris and Finch[4] reported the density and refractive index of this sulfone. Although studies concerning this sulfone have been reported by Frank,[5] Drake,[6] and Grummitt and co-workers[7] no characterization of the compound was reported. Thus, the first objective of the present work is the purification and characterization of I. The sulfone was prepared by the reaction of sulfur dioxide and 1,3-pentadiene in the presence of hydroquinone, to give a colorless oil in 55% yield. Purification of I was effected by distillation at reduced pressure in an atmosphere of sulfur dioxide or more simply by the method described in detail in the Experimental section of this paper. The latter method was found to give as good a product and one which exhibits practically no absorption in the ultraviolet between 220 and 320 mμ at concentrations up to 1 g./liter in ethanol. The crude sulfone, as it moved through the purification scheme, showed a steady decrease in absorption at 220–230 and 280–300 mμ. The loss of absorptivity in these regions was found to be due to removal of traces of 1,3-pentadiene and sulfur dioxide, respectively. The infrared spectra of the distilled sulfone and the extracted sulfone are in excellent agreement.

Under refrigeration at 0° the decomposition of the purified sulfone becomes perceptible through the odor of sulfur dioxide after 11 days, and the sulfone undergoes complete dissociation at 100°. Previous studies in this laboratory demonstrated the utility of bromine adducts as aids in the characterization of certain unsaturated sulfones, hence, the dibromide from I was prepared. Actually, two dibromides from I appear to have been obtained, and it is suggested that these two dibromides are two racemic mixtures. The higher melting dibromide will be referred to as IIa and the lower melting substance as IIb. Sulfone I as well as adducts IIa and IIb are optically inactive; however, if one assumes the trans addition of bromine (see reaction conditions) to sulfone I four stereoisomers are indeed possible (two racemic mixtures). Quantitative analysis supports the formula $C_5H_8Br_2O_2S$ for IIa and IIb. While the infrared spectra of IIa and IIb are similar, the spectra are definitely not identical. Sulfone I was converted to the tetrahydro derivative, 2-methyltetrahydrothiophene 1,1-dioxide (III) in 91% The physical constants for III are in good agreement with those reported by Grishkevich-Trokhimovskii[8] who prepared this compound by the reaction of 1,4-dibromopentane and sodium sulfide, and the subsequent oxidation of the cyclic sulfide of the sulfone. The infrared spectrum of III appears in good agreement with the spectra of 3-methyltetrahydrothiophene 1,1-dioxide and with

(1) American Chemical Society Graduate Fellow. This research was supported by a grant from The Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of said fund.

(2) For the previous paper see R. C. Krug, G. R. Tichelaar, and F. E. Didot, *J. Org. Chem.*, **23**, 212 (1958).

(3) D. Craig, *J. Am. Chem. Soc.*, **65**, 1006 (1943).

(4) R. C. Morris and H. deV. Finch (to Shell Development Co.), U. S. Patent **2,373,329**, April 10, 1945.

(5) E. J. Frank, *J. Am. Chem. Soc.*, **69**, 2313 (1947).

(6) S. P. Drake, *J. Am. Chem. Soc.*, **68**, 2521 (1946).

(7) O. Grummitt, A. E. Ardis, and J. Fick, *J. Am. Chem. Soc.*, **72**, 5167 (1950).

(8) E. Grishkevich-Trokhimovskii, *J. Russ. Phys. Chem. Soc.*, **48**, 901 (1916).